## SOLID PHASE EXTRACTION-GAS CHROMATOGRAPHY/ MASS SPECTROMETRY METHOD

A solid phase extraction (SPE)-gas chromatography/mass spectrometry (GC/MS) method was developed for quantifying several of the targeted DBPs for this study (Figure 1). SPE offers an alternative extraction means to conventional liquid-liquid extraction, and the use of a mass spectrometric detector provides specificity that is not possible with electron capture detection (ECD) included in EPA Method 551.1. With the method developed here, concentration of 100 mL of drinking water by SPE provided a sufficient concentration factor to achieve low µg/L detection.

## EXPERIMENTAL

### Instrumentation

A Varian Saturn 2000 ion trap mass spectrometer (Varian Analytical Associates Inc., Walnut Creek, CA) equipped with a 3800 GC and a CTC A200s autosampler (CTC Analytics, Switzerland) was used. Early methods development was performed on a VG TS-250 medium-resolution mass spectrometer (VG Tritech – now Micromass, Inc., Manchester, England). A Hewlett-Packard/Agilent Model 5890 GC (Palo Alto, CA) was used for separations and was partially controlled by an Optic 2 injector (AI Cambridge Ltd., Cambridge, England). Both full-scan and selected ion monitoring (SIM) analyses were conducted.

### Sample Preparation

Varian Bond Elut PPL (Varian Associates, Inc., Harbor City, CA) SPE cartridges were used for extraction of drinking water. Certified standard mixtures were obtained from Ultra Scientific (North Kingstown, RI). HCM-551B contains the following compounds at a level of 5000 µg/mL in acetone: bromochloroacetonitrile, chloropicrin, dibromoacetonitrile, dichloroacetonitrile, 1,1-dichloropropanone, trichloroacetonitrile, and 1,1,1-trichloropropanone. THM-521 mix contains chloroform, bromodichloromethane, dibromochloromethane, and bromoform at a level of 5000 µg/mL in methanol.

For the DBPs investigated in this study, stock solutions were prepared by accurately measuring 1.0 mL of methanol (Burdick & Jackson, purge and trap grade, Muskegon, MI) into a capped 1.4 mL autosampler vial and weighing it. Approximately 2-3 µL of pure standard were pulled into a clean syringe and spiked under the solvent after piercing the septum. The additional weight by difference, between 2-5 mg, was used to calculate an approximate concentration value. Alternatively, solid compounds were weighed by difference and deposited directly into an empty autosampler vial before solvent was added. The septum caps were changed before storage of the samples. Using diluted versions of these stock solutions, the purity of the stock solutions could be obtained, and adjustments made to the initial calculations (see separate section on Standards).

SPE was performed using a commercially available 12-port Visiprep vacuum manifold and 1/8-inch Teflon tubing with weighted stainless steel ends (Supelco Chromatography, Bellafonte, PA). Samples (100 mL) were placed in clean and dry 125-mL Erlenmeyer flasks that had been rinsed several times in pure water and baked for 1 hour at 130 ºC. The Teflon tubing was heated for 10 min at 130 ºC.

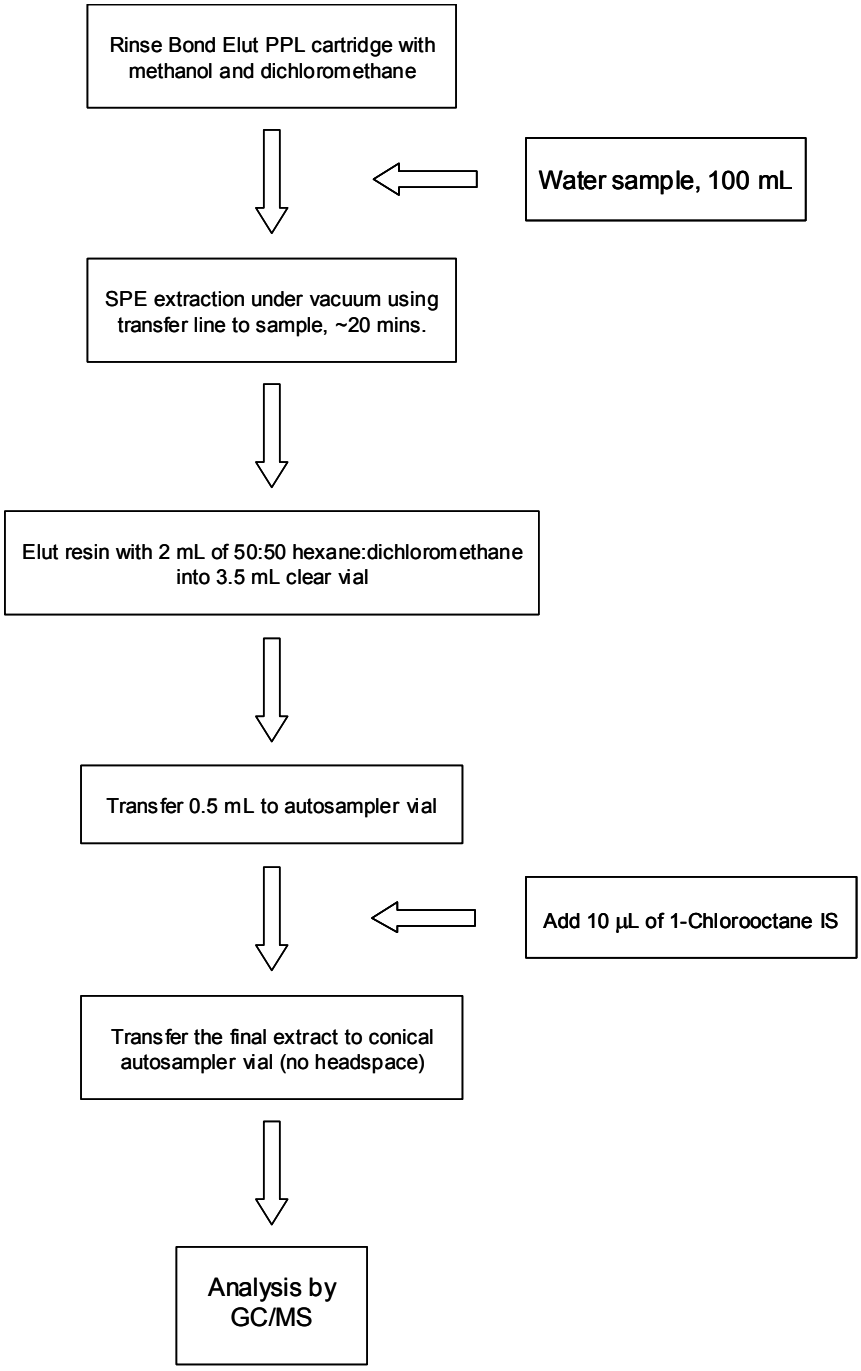


**Figure 1. Summary of the SPE-GC/MS method used for analyzing 35+ DBPs in drinking water.**

Six 3-mL SPE cartridges were conditioned by adding two 3 mL aliquots of methanol to the cartridge and allowing it to drain under vacuum, followed by two 3 mL aliquots of dichloromethane (Mallinckrodt Baker Inc., Paris, Kentucky). The samples were then attached to the vacuum manifold using the Teflon tubing and tube adapters. The flow rates were between 2 and 7 mL/minute for all samples for complete passage of the water through the sorbent. The vacuum lines were closed individually upon completion of the water transfer. To avoid loss of compounds, the vacuum was not applied to the sorbents any longer than necessary once the water had eluted.

The Teflon tubing from each sample cartridge was removed and the vial rack inserted with six 3.5-mL collection vials. Two mL of a 1:1 mixed solvent system of hexane (Aldrich Chemical Co., THM grade, Milwaukee, WI) and dichloromethane was used as the elution solvent and placed at the top of the sorbent. (It was not possible to use MtBE as a solvent, due to the Varian ion trap mass spectrometer being located in a MtBE-free environment in the laboratory). The individual manifold valves were opened and 10 drops were allowed to pass through the sorbent material. The six samples were eluted sequentially, 10 drops at a time, until no solvent was left in the cartridge. To complete the procedure, 0.5 mL of the top portion phase was transferred to an autosampler vial capped with a Teflon-lined septum. Ten µL of a 10 mg/L 1-chlorooctane standard (Chem Service, West Chester, PA) was added as the internal standard.

**Standards and Check Sample**

One advantage of a sector-based mass spectrometer is the dynamic range that can be achieved. Unlike an ion trap mass spectrometer, ions are separated in space and do not suffer from so-called "space charge" phenomena. Beginning with the first St. Louis/East St. Louis sample set (January 2001), a protocol was established that included standards made at the following levels: 1.0, 2.5, 5.0, 10, 20, 30, 40, 50, 60, 75, and 100 µg/L in pure water and adjusted to pH 3.5 (for initial analyses using the TS-250 sector mass spectrometer). These higher values (up from 40 µg/L previously) were used to bracket some of the higher THM concentrations that were seen at some earlier utilities. It was not feasible to spike a mixed set of DBPs for any given standard because of software processing limitations. Any higher concentration data points that were skewing the calibration curve or causing undesirable effects were eliminated. Using this method, very linear curves were produced for most of the 43 compounds analyzed by SPE-GC/MS.

The “check standard” can either be a newly extracted standard or a reinjection of one of the calibration standards. For the early utilities, the original calibration standards were used as check standards because it was very important to make sure that the instrument response had not drifted over the extended runs of the instrument (up to 38 hours). The final check was typically a 50 µg/L or 40 µg/L standard that was used to prove the instrument was still responding correctly. In this way, the check standard was certifying the run, and not necessarily the method.

New calibration standards were required to address the inability to use MtBE as the primary solvent for the SPE method. Migrating the method to the Varian ion trap mass spectrometer also set restrictions on the concentration range of standards that could be run on the instrument to avoid saturation of the trap and potential carryover to subsequent samples. Careful evaluation of the ion trap's sensitivity at full scan led to the following recommendations for standard concentrations: 0.25, 0.50, 1.0, 2.5, 5.0, 7.5, 10, 15, 20, 30, and 40 µg/L. Only the

range 0.25 µg/L to 30 µg/L would be used for calibration purposes because of a ten-point limit with the Star Workstation software. The 40 µg/L standard would be used for optional processing should THM concentrations exceed this range. This became an acceptable protocol because all DBP concentrations typically were below 40 µg/L, with the exception of chloroform, which was later dropped from the SPE method due to co-elution with the 1:1 hexane:methylene chloride solvent system. The final check standard and all sample spikes were at a level of 10 µg/L.

**Gas Chromatography**

Prior to June 2001, when the TS-250 sector mass spectrometer was used, the primary column was a DB-1, 30-m, 0.25-mm ID column with a 1-µm film thickness (J & W Scientific/Agilent, Folsom, CA). The Optic 2, an advanced programmable temperature injector unit, was used to develop the EPA method in conjunction with the TS-250 mass spectrometer. The unit comes with its own injector replacement for the Hewlett Packard 5890 GC and controls the flow of helium carrier gas, the injection temperature, and the split valves. The Optic 2 injector was set at 110 $^{o}$C and was operated in a splitless mode with a head pressure of 8.0 psi on the column. Injection volume was 3 µL. The temperature program followed EPA Method 551.1: 1) Hold at 35 ºC for 22 min; 2) increase to 145 ºC at 10 ºC/min and hold at 145 ºC for 2 min; and 3) increase to 225 ºC at 20 ºC/min and hold at 225 ºC for 10 min.

After June 2001, when the Saturn ion trap mass spectrometer was used, the primary column was a DB-1, 30-m, 0.25-mm ID column with a 1-µm film thickness (J & W Scientific/Agilent, Folsom, CA). The Model 1079 injector was set at 90 $^{o}$C and was operated in a splitless mode. Injection volume was 3 µL. The temperature program was changed to match the LLE-GC/ECD method being developed: 1) Hold at 35 ºC for 23 min; 2) increase to 139 ºC at 4 ºC/min; and 3) increase to 301 ºC at 27 ºC/min and hold at 301 ºC for 5 min. This program will be referred to as the updated GC program.

**Mass Spectrometry**

Electron ionization (EI) spectra show similar fragmentation patterns depending on the class of compound (Table 1). Using a defined sample list and methodology, software is capable of integrating individual channels to extract out the peaks of interest. After peak integration, the resulting areas are used to form calibration curves for each compound, which can then be applied to unknown samples.

Selected ion monitoring was used to achieve greater sensitivity with the TS-250 mass spectrometer. Because the DBPs measured are less than a few hundred Daltons in mass and contain similar functional groups, it was possible to monitor selected ion traces that comprised common fragment ions for all the compounds. This provided a significant enhancement in sensitivity for the older TS-250 sector mass spectrometer.

**Table 1. Fragmentation matrix for DBPs measured using selected ion monitoring. A bold "X" indicates the quantitation ion; "$x_c$" is the confirmation peak. A strike through the x indicates a false peak.**

| Compound | Identified Fragment in EI Spectrum | | | | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 40 | 43 | 49 | 74 | 75 | 77 | 79 | 83 | 91 | 93 | 108 | 117 | 118 | 119 | 120 | 121 | 127 | 130 | 154 | 163 | 173 | 175 | 198 | 207 | 219 | 251 | 267 |
| **Halomethanes** | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Chloroform | | | $x_c$ | | | | | X | | | | | | | | | | | | | | | | | | | |
| Bromodichloromethane | | | x | | | | $x_c$ | X | | | | | | | | | x | | | | | | | | | | |
| Dibromochloromethane | | | x | | | | x | | $x_c$ | x | | | | | | | X | | | | | | | | | | |
| Bromoform | | | | | | | x | | $x_c$ | x | | | | | | | | | | | X | x | | | | | |
| Tribromochloromethane | | x | x | | | | $x_c$ | | x | x | | | | | | | | x | | | | | | X | | x | |
| Bromochloroiodomethane | | | | | | | x | | | | | | | | | | X | | | | | $x_c$ | | | | | |
| Dichloroiodomethane | | | x | | | | | X | | | | | | | | | $x_c$ | | | | | x | | | | | |
| Dibromoiodomethane | | | | | | | x | | x | x | | | | | | | $x_c$ | | | | X | x | | | x | | |
| Chlorodiiodomethane | | | | | | | | | | | | | | | | | $x_c$ | | | | | X | | | | | x |
| Bromodiiodomethane | | | | | | | x | | | | | | | | | | $x_c$ | | | | | | | | X | | x |
| Iodoform | | | | | | | | | | | | | | | | | X | | | | | | | | | | $x_c$ |
| **Haloacetonitriles** | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Bromoacetonitrile | x | | | | | | $x_c$ | | x | x | | | | X | | x | | | | | | | | | | | |
| Chloroacetonitrile | x | | | | X | ~~x~~ | | | | | | | | | | | | | | | | | | | | | |
| Dichloroacetonitrile | | | $x_c$ | X | x | x | | | | | | | | | | | | | | | | | | | | | |
| Bromochloroacetonitrile | | | x | X | x | x | x | | | | | | x | | | | | | | | | | | | | | |
| Dibromoacetonitrile | | | | | | | $x_c$ | | x | x | | | X | | x | | | | | | | | | | | | |
| Trichloroacetonitrile | | | $x_c$ | | x | | | | | | X | | | | | | | | | | | | | | | | |
| Tribromoacetonitrile | | | | | | | $x_c$ | | x | x | | x | x | x | | | | | | | | | X | | | | |
| Bromodichloroacetonitrile | | | x | x | x | | x | | x | x | X | x | | x | | | | x | $x_c$ | | | | | | | | |
| Dibromochloroacetonitrile | | | x | $x_c$ | x | | x | | x | x | | x | x | x | x | | | | X | | | | x | | | | |
| **Haloketones** | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Chloropropanone | | X | $x_c$ | | | | | | | | | | | | | | | | | | | | | | | | |
| 1,1-Dichloropropanone | | X | x | | | | | x | | $x_c$ | | | | | | | | | | | | | | | | | |
| 1,3-Dichloropropanone | | x | $x_c$ | | | X | x | | | | | | | | | | | | | | | | | | | | |
| 1,1,1-Trichloropropanone | | X | x | | | | | $x_c$ | | | x | | | x | | | x | | | | | | | | | | |
| 1,1,3-Trichloropropanone | | | x | | | X | x | $x_c$ | | | | | | | | | | | | | | | | | | | |
| 1,1,3,3-Tetrachloropropanone | | | x | | | | | X | | | | | | | | | | | | | | | x | | | | |
| 1,1,1,3,3-Pentachloropropanone | | | x | | | | | X | | | | $x_c$ | | x | | x | | | | | | | | | | | |
| 1-Bromo-1,1-dichloropropanone | | X | x | | | x | x | x | | | | | | | | | $x_c$ | | | x | | | | | | | |
| 1,1-Dibromopropanone | | X | | | | | x | | x | x | | | | | x | | | | | | x | x | | | | | |
| 1,3-Dibromopropanone | | x | | | | | | | | $x_c$ | | | | | | X | | | | | | | | | | | |
| 1,1,1-Tribromopropanone | | X | | | | | x | | $x_c$ | x | | | | | | | | | | | x | x | | | | x | |
| 1,1,3-Tribromopropanone | | x | | | | | x | | x | $x_c$ | | | | | x | X | | | | | x | x | | | | | |
| 1,1,3,3-Tetrabromopropanone | | | | | | | | | | | | | | | X | | | | | | x | x | | | | | |
| **Haloacetaldehydes** | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Dichloroacetaldehyde | | | X | | | x | | $x_c$ | | | | | | | | | | | | | | | | | | | |
| Bromochloroacetaldehyde | | | X | | | | x | | x | x | | | | | | | x | $x_c$ | | | | | | | | | |
| Tribromoacetaldehyde | | | | | | | $x_c$ | | x | x | | | | | | | | | | | X | x | | | | x | |
| **Halonitromethanes** | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Chloronitromethane | | | X | | | | | | | | | | | | | | | | | | | | | | | | |
| Bromonitromethane | | x | | | | | $x_c$ | | | X | | | | | | | | | | | | | | | | | |
| Dichloronitromethane | | | | | | | | X | | | | | | | | | | | | | | | | | | | |
| Dibromonitromethane | | $x_c$ | | | | | x | | x | x | | | | | | | | | | | X | x | | | | | |
| Chloropicrin | | | $x_c$ | | | x | | | | | | X | | ~~X~~ | | x | | | | | | | | | | | |
| Bromopicrin | | | | | | | x | | $x_c$ | x | | | | | | | | | | | | | | | | x | |
| Bromodichloronitromethane | | | $x_c$ | | | | x | | x | x | | | | | | | | | | x | | | | | | | |
| Dibromochloronitromethane | | | x | | | | $x_c$ | | x | x | | | | | | | | | | | | | | X | | | |
| **Misc. Compounds** | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Carbon tetrachloride | | | $x_c$ | | | | | | | | | X | | ~~X~~ | | x | | | | | | | | | | | |
| Benzyl chloride | | | | | | | | | X | | | | | | | | | | | | | | | | | | |

## Sample Preservation

As samples are taken in the field, it is necessary to stop any further DBP formation from occurring by adding a quenching agent that can remove residual oxidants. In previous work, dilute solutions of ascorbic acid (AA) or ammonium chloride (AC) were added directly to the sample vial or bottle. This method works well, provided that the containers are not allowed to sit idle for more than a few days. Additionally, past studies have found that by adjusting the pH of the sampled water, many DBPs can be stabilized for several weeks, giving a much larger window of opportunity for analysis and establishing a better holding time for refrigerated storage.

The method parameters chosen for this study were 31 mg/L of ascorbic acid and enough sulfuric acid to lower the pH to 3.5. A solution of 16 mg/L of ascorbic acid was deemed necessary to remove 3.0 mg/L of chloramines residual, so 31 mg/L of ascorbic acid in each bottle was chosen to have a safety factor. An experiment was performed on Weymouth effluent water from the Weymouth Water Treatment Plant (La Verne, CA) using clear 44-mL vials with 1.4 mg of ascorbic acid (31 mg/L) and 5 drops of 0.25 M $H_2SO_4$ added. The 5 drops were enough to fully dissolve the ascorbic acid powder. After several days, however, the contents of the vials proved ineffective for quenching fresh samples of water. This posed a problem because the ascorbic acid in the acidic solution was degrading. As a result, the ascorbic acid and sulfuric

acid would have to be separated. Separate additions of ascorbic acid and sulfuric acid was also wise because it would be difficult to know the appropriate dose of acid to achieve the required pH for water utilities where the buffering capacity of the water was unknown. It was decided that an acid kit, which would include an eyedropper bottle with dilute sulfuric acid and pH test strips, would accompany each set of ice chests sent to the utilities, so that the sampler operators could add the necessary acid in the field. The quenching agent, ascorbic acid, in its granular form, would be added to each container at the Metropolitan Water District of Southern California (MWDSC) before shipping. For the 125 mL bottles filled for SPE-GC/MS analysis, two 2 mg scoops were used to achieve the ~4.0 mg and a solution concentration of 31 mg/L.

Each utility was given a detailed set of instructions and told not to rinse out the bottles (because they contained preservative). Only vials and bottles containing a red cap would require pH adjustment with acid. This situation worked out well because when unforeseen delays arose for the utility sampling, the bottles could be kept for several weeks both before the sampling and after the sampling without compromising the DBP preservation. When samples returned to the laboratory, their pH was re-checked and adjusted if necessary.

### Ice Chest Containers

When each of the ice chests was opened, there was a set of paperwork immediately on top (sampling instructions, sample collection sheets, and a return Federal Express label). There was a sheet attached to the inside of each ice chest identifying it as belonging to the MWDSC and labeling the appropriate utility to which it was sent. Additional information included the identification of ice chests intended for simulated distribution system (SDS) samples or assimilable organic carbon (AOC) samples. The large ice chests contained four blue ice packs. The small ice chests contained one or two ice packs, depending on space. All ice packs were shielded from the sample bags by Styrofoam, peanut-filled plastic bags. It was important to isolate the cold packs from the samples to prevent freezing of the water and breakage.

The sulfuric acid solution containers were placed in small white boxes located usually along with the SDS ice chests. These acid kits included an eyedropping amber bottle, two additional plastic eyedroppers in case of breakage, and a set of pH test strips.

## RESULTS AND DISCUSSION

### Detection Limits

*TS-250 Mass Spectrometer.* Because the TS-250 instrument was older and was subject to drift during the course of a day's analysis, calibration standards were run with each set of samples to insure the most accurate results. A set of three 10 µg/L standards, comprising 20 of the DBPs, were extracted using SPE and analyzed the same day on three separate occasions. The results were interpreted for daily standard deviation and for the overall standard deviation for all 9 samples. The overall standard deviation was multiplied by 2.896 (student t-value for 8 degrees of freedom at 98% confidence) to get the approximate method detection level (Table 2).

A daily precision of 1.1 µg/L was observed for samples that underwent off-line SPE. However, when comparisons were made of data taken over multiple days, this variance increased to 2.2 µg/L. Overall detection limits were set at 3 µg/L because of the requirement that

standards be run on a daily basis. This limit appeared reasonable because the instrument was capable of detecting 1 µg/L levels.

The solid phase extraction technique is probably at its limit for reproducibility (for low ppb levels). SPE, unlike P&T, is performed manually over the course of several hours. Human error will play some role in the extraction process, but there is also a significant time segment where the sample is either exposed to a hood environment or direct vacuum, which can potentially contribute to the loss of some compounds.

Errors in quantitation of samples can also occur due to the SIM scan speed of the magnet. For SIM acquisition, the dwell time for each m/z measurement must be sufficiently long to adequately sample the ion population, but sufficiently short to collect as many samples per eluting peak as possible. By setting a residence time of 50 msec per m/z measured and allowing time for the magnet to switch to next mass, there is a necessary scan time of 2.17 seconds/scan. Often, this amounts to only 5 to 8 samples per chromatographic peak, which can cause errors because a peak area approximated by only 5 to 8 data points will be inherently less accurate than one sampled by many more points to give better peak resolution.

**Table 2. Detection limit study for selected compounds showing both daily and overall standard deviations for a typical 10 µg/L standard**

| Compound | RT | A | B | C | D | E | F | G | H | I | Daily Std. Deviation | | | AVE | SD | RSD | Estimated |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | (min.) | 4/10 | 4/10 | 4/10 | 4/12 | 4/12 | 4/12 | 4/18 | 4/18 | 4/18 | 4/10 | 4/12 | 4/18 | Conc. | AVE | % | MDL, ug/L |
| Chloroform | 5.98 | 9.0 | 9.4 | 9.7 | 5.9 | 6.2 | 6.3 | 8.6 | 9.5 | 10.1 | 0.4 | 0.2 | 0.8 | 8.3 | 1.7 | 20 | 5 |
| Dichloroacetaldehyde | 6.20 | 17.7 | 15.2 | 16.2 | 13.7 | 13.0 | 13.9 | 9.6 | 11.5 | 11.2 | 1.3 | 0.5 | 1.0 | 13.6 | 2.6 | 19 | 7 |
| Chloroacetonitrile | 7.46 | 9.9 | 12.7 | 14.7 | 11.7 | 13.7 | 13.3 | 8.4 | 12.2 | 12.4 | 2.4 | 1.1 | 2.3 | 12.1 | 1.9 | 16 | 6 |
| Chloropropanone | 8.15 | 6.2 | 7.1 | 13.3 | 12.1 | 12.8 | 13.5 | 11.6 | 11.7 | 13.9 | 3.9 | 0.7 | 1.3 | 11.4 | 2.8 | 25 | 8 |
| Trichloroacetonitrile | 8.80 | 10.3 | 10.5 | 10.7 | 5.6 | 6.1 | 5.9 | 7.7 | 8.5 | 8.9 | 0.2 | 0.3 | 0.6 | 8.2 | 2.0 | 25 | 6 |
| Dichloroacetonitrile | 10.17 | 10.7 | 11.1 | 12.1 | 8.3 | 10.0 | 10.4 | 7.5 | 9.0 | 10.9 | 0.7 | 1.1 | 1.7 | 10.0 | 1.5 | 15 | 4 |
| Bromodichloromethane | 10.50 | 9.3 | 9.7 | 10.4 | 5.8 | 6.9 | 6.8 | 7.8 | 8.9 | 10.3 | 0.6 | 0.6 | 1.3 | 8.4 | 1.7 | 20 | 5 |
| 1,1-Dichloropropanone | 12.70 | 9.1 | 9.6 | 10.1 | 9.2 | 10.3 | 10.9 | 8.0 | 9.9 | 11.1 | 0.5 | 0.9 | 1.6 | 9.8 | 1.0 | 10 | 3 |
| Bromoacetonitrile | 14.50 | 10.6 | 12.5 | 13.9 | 11.9 | 13.8 | 15.5 | 6.5 | 9.7 | 11.8 | 1.7 | 1.8 | 2.7 | 11.8 | 2.7 | 23 | 8 |
| Chloropicrin | 19.81 | 10.5 | 10.2 | 11.1 | 4.6 | 5.7 | 5.9 | 6.9 | 8.4 | 9.4 | 0.5 | 0.7 | 1.3 | 8.1 | 2.4 | 29 | 7 |
| Dibromochloromethane | 20.61 | 10.3 | 10.5 | 11.4 | 5.8 | 7.4 | 7.6 | 6.5 | 9.1 | 10.7 | 0.6 | 1.0 | 2.1 | 8.8 | 2.0 | 23 | 6 |
| Bromonitromethane | 21.00 | 11.6 | 12.3 | 13.7 | 8.3 | 11.9 | 13.5 | 5.9 | 9.2 | 10.6 | 1.1 | 2.7 | 2.4 | 10.8 | 2.6 | 24 | 7 |
| Bromochloroacetonitrile | 21.26 | 11.7 | 11.9 | 12.8 | 7.9 | 9.8 | 10.0 | 6.4 | 8.4 | 9.9 | 0.6 | 1.2 | 1.8 | 9.9 | 2.1 | 21 | 6 |
| 1,1,1-Trichloropropanone | 26.38 | 11.9 | 12.2 | 12.9 | 9.0 | 10.4 | 10.9 | 6.3 | 8.6 | 10.0 | 0.5 | 1.0 | 1.9 | 10.2 | 2.1 | 20 | 6 |
| 1,3-Dichloropropanone | 27.14 | 12.5 | 13.9 | 14.4 | 11.2 | 12.0 | 13.5 | 4.8 | 8.7 | 9.6 | 1.0 | 1.2 | 2.6 | 11.2 | 3.1 | 27 | 9 |
| Bromoform | 28.12 | 10.9 | 11.2 | 12.4 | 6.8 | 8.7 | 8.9 | 6.4 | 8.7 | 10.3 | 0.8 | 1.2 | 2.0 | 9.4 | 2.0 | 21 | 6 |
| Dibromoacetonitrile | 28.48 | 12.3 | 12.6 | 13.3 | 7.9 | 9.5 | 10.0 | 6.4 | 7.8 | 9.2 | 0.5 | 1.1 | 1.4 | 9.9 | 2.4 | 24 | 7 |
| 1,1,3-Trichloropropanone | 30.75 | 16.4 | 14.8 | 15.4 | 11.3 | 11.6 | 10.8 | 8.3 | 9.9 | 9.0 | 0.8 | 0.4 | 0.8 | 11.9 | 2.9 | 24 | 8 |
| Benzyl Chloride | 32.66 | 10.3 | 10.6 | 11.6 | 6.9 | 8.1 | 8.4 | 5.9 | 7.1 | 7.8 | 0.7 | 0.8 | 1.0 | 8.5 | 1.9 | 22 | 6 |
| Iodoform | 37.86 | 12.4 | 12.7 | 13.3 | 7.2 | 8.2 | 8.2 | 10.2 | 9.6 | 9.3 | 0.5 | 0.6 | 0.5 | 10.1 | 2.2 | 22 | 6 |
| | | | | | | | | **Averages** | | | **1.0** | **1.0** | **1.6** | | **2.2** | **21.5** | **6.3** |

**Extraction Efficiency**

The extraction efficiency of the Bond Elut sorbent was tested at three different standard concentrations, 10 µg/L, 25 µg/L, and 50 µg/L, to determine whether there were any sample loading concerns with the sorbent's capacity. Most of the anticipated values for DBPs in drinking water would be well below 50 µg/L. Compounds within the same compound family exhibited similar extraction efficiencies. The important observations were that recoveries were good (74% average) and higher concentrations of analytes, up to 500 µg/L, do not saturate the capacity of the Bond Elut sorbent.

**Early Observations**

VOC concentrations can become altered if excessive headspace or high temperatures are present. For analysis, the headspace was minimized by using 100 µL conical autosampler vials (that hold ~300 µL when filled to top) for storage, rather than the typical 1.4 mL autosampler vials. For samples that sit on top of the GC for extended runs, they are exposed to high temperatures. A Tekmar water bath circulating system was attached to the sample tray to remove some of the heat load. The water bath's temperature was set to maintain a temperature of 21.0 $^{o}$C (about room temperature) on the sample tray, which minimized sample degradation/volatilization for extended runs. Chloroform and bromodichloromethane showed the most improvement for spike recovery.

The heavier iodo-THMs, haloacetonitriles, and halonitromethanes showed much reduced recoveries for 10 ppb-spiked samples. This was either an expected limitation for the SPE procedure, or the lower injection temperature used discriminated against these heavier (higher boiling point) compounds. Significantly raising the injection temperature, however, would have caused many more problems with degrading species. It was discovered later that some of these compounds (bromodichloro-, dibromochloro-, and tribromoacetonitrile, and bromodichloro-, dibromochloro-, and tribromonitromethane) were not preserved using ascorbic acid.

Several analytes were found to coelute on the GC. Bromochloroacetaldehyde (retention time of 12.6 min.) co-eluted with trichloroacetaldehyde, which was not present in the method, but has been seen in many samples and was part of the Information Collection Rule. Chloropicrin (retention time of 21.8 min.) co-eluted with bromodichloroacetonitrile. An easy separation was achieved by using different quantitation masses -- m/z 117 for chloropicrin and m/z 108 for bromodichloroacetonitrile. The m/z 117 contribution from bromodichloroacetonitrile, if present, was negligible and small enough to ignore.

Tribromoacetaldehyde (retention time of 32.8 min.) co-eluted with tribromoacetonitrile. An alternate quantitation peak, m/z 251, was chosen for tribromoacetaldehyde, at reduced sensitivity, to effect a clean separation from tribromoacetonitrile and other nearby species. Bromonitromethane was sandwiched between dibromochloromethane and bromochloroacetonitrile, which did not allow baseline resolution for that quantitation channel, m/z 93.

Dibromoiodomethane, 1,3-dibromopropanone, tribromoacetaldehyde, and tribromoacetonitrile all eluted within 0.1 min of each other. Alternate channels eliminated major overlaps, but sensitivity was reduced. Chloro-, 1,1-dichloro-, 1,1,1-trichloro-, 1,1-dibromo-, 1-bromo-1,1-dichloro-, and 1,1,1-tribromopropanone were difficult to quantitate because of

common fragmentation patterns produced. The highest ion abundance came from m/z 43 ($COCH_3$), which showed a low level persistent background throughout the run. Another co-eluting system -- dibromoacetonitrile/bromodichloronitromethane (retention time of 33.9 min.) -- was eliminated by using different mass channels. Improved chromatography or the use of a different polarity column could also correct this problem.

**Choice of Analytical Columns**

*CP-1301 Column.* The CP-1301 column was installed on the TS-250 mass spectrometer to evaluate its performance for separating the targeted DBPs. The GC temperature program was the latest that MWDSC had been using, with the exception that this column could not go beyond a maximum temperature of 250 $^{o}$C. This lowered maximum temperature caused a lower overall sensitivity for late eluting compounds.

Peaks that were not baseline-resolved included dichloronitromethane and dibromochoromethane, bromoacetonitrile and dichloroiodomethane, and bromochloronitromethane and bromoform. Another difficult problem was that of co-eluting species, which for the CP-1301 column included: chloroform + others, carbon tetrachloride + others, dichloroacetonitrile + bromodichloroacetonitrile, 1,1-dibromopropanone + bromochloroiodomethane, and dibromoiodomethane + benzyl chloride. Peaks for dichloroacetaldehyde, bromochloracetaldehyde, trichloroacetaldehyde, tribromonitromethane, and 1,1,3,3-tetrabromopropanone were not found, or, they were problematic for analysis using this column/setup. Bromodichloronitromethane and dibromochloronitromethane were not included in this mixture analyzed. Figure 2 shows the CP-1301 column performance for the targeted DBPs.

*DB-5 Column.* A DB-5 column was installed on the TS-250 mass spectrometer and was used to analyze the same spiking mixture. There were a lot of co-eluting peaks, although it was clear that trichloroacetaldehyde and bromochloroacetaldehyde were well separated. Another benefit of this column was that there was better signal-to-noise, compared to the CP-1301 column, particularly at the high end of the chromatogram where degradation of compounds and column bleed is normally a problem.

Peaks that were not baseline resolved included bromochloronitromethane and 1,1,1-trichloropropanone; 1,1,3-trichloropropanone and tribromochloromethane; and 1,1,1-tribromopropanone and bromodiiodomethane. Co-eluting peaks included dichloroacetaldehyde + others; chloroacetonitrile + trichloroacetonitrile; bromonitromethane + bromochloroacetonitrile; dibromoiodomethane + tribromoacetonitrile + benzyl chloride; and chlorodiiodomethane + 1,1,3,3-tetrachloropropanone.

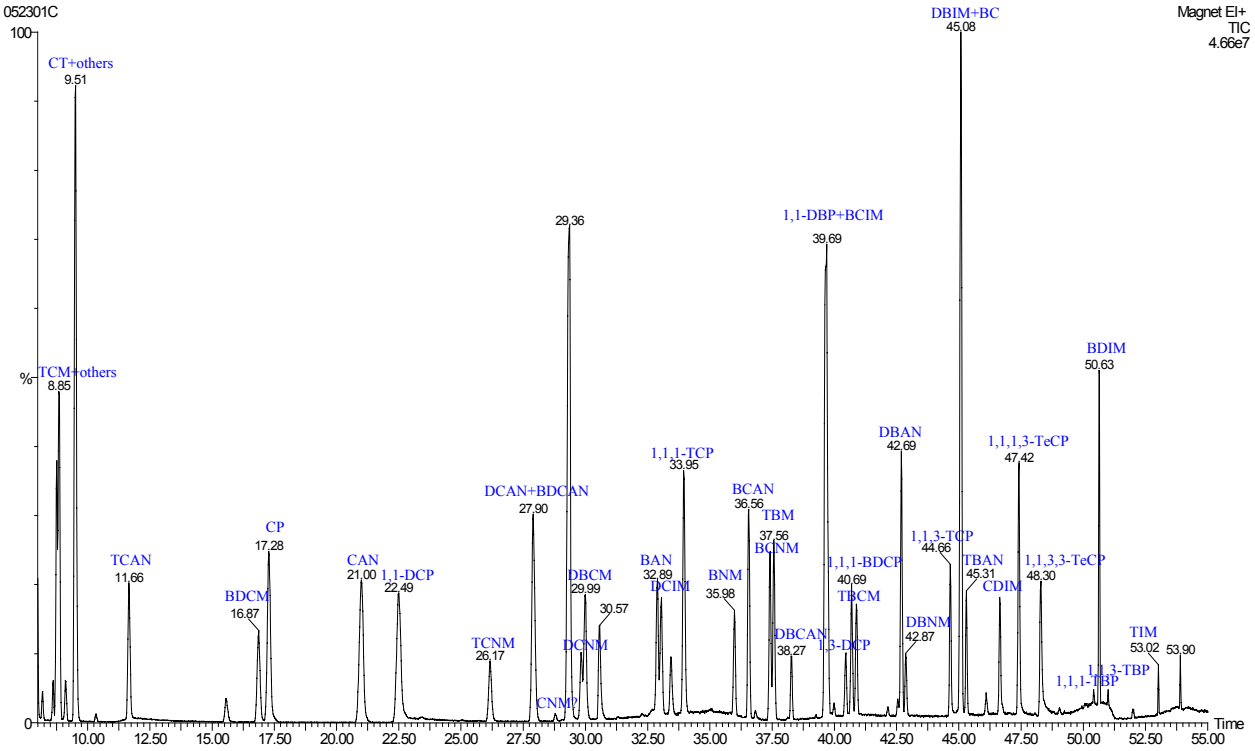


**Figure 2. CP-1301 column performance using full DBP set. Compounds not detected include dichloroacetaldehyde, bromochloroacetaldehyde, tribromoacetaldehyde, tribromonitromethane, and 1,1,3,3-tetrabromopropanone. Compound abbreviations are found in Table 3.**

*DB-1 Column*. As a comparison between the DB-5 column and a DB-1 column, the two columns are profiled side-by-side in Figure 3**,** which shows unambiguous peak identities when converting between the two chromatograms. As a general rule, the DB-1 column was preferred because, in conjunction with individual mass traces, it allowed for the separation of all the targeted DBPs, except for the trichloroacetaldehyde-bromochloroacetaldehyde conflict. In general, DB-1 improvements over DB-5 included: a) separation of chloroacetonitrile and trichloroacetonitrile, b) separation of bromonitromethane and bromochloroacetonitrile, c) separation of bromochloronitromethane and 1,1,1-trichloropropanone, d) separation of 1,1,3-trichloropropanone and tribromochloromethane, e) partial separation of dibromoiodomethane, tribromoacetonitrile, and benzyl chloride, f) separation of chlorodiiodomethane and 1,1,3,3-tetrachloropropanone, and g) separation of 1,1,1-tribromopropanone and bromodiiodomethane.

*DB-624 Column*. The DB-624 column used on the Varian Saturn ion trap mass spectrometer was very similar in polarity to the CP-1301 column tested. It is the column currently used by MWDSC for the EPA Method 524.2 purge-and-trap analyses. Many of the heavier DBPs, such as the halonitromethanes were not well recovered from this column, partially due to the polarity and lowered maximum temperature. The DB-624 column was replaced with a DB-1 column to achieve the same performance, as was being done for the LLE-GC-ECD and SPE-GC/MS (TS-250 mass spectrometer) methods. The replacement option made it necessary

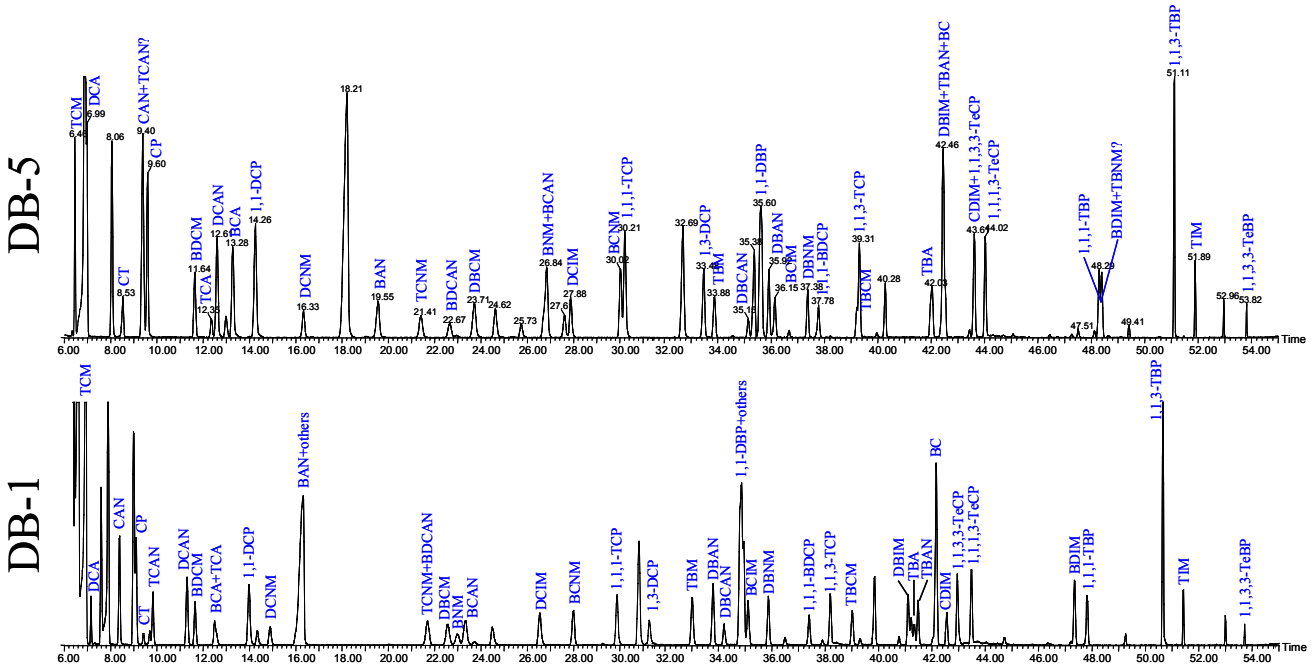


**Figure 3. DB-5 column versus DB-1 column performance using full DBP set.**

to re-evaluate purge-and-trap operation with a DB-1 column for a more limited set of compounds.

## Improved Temperature Program

The updated GC temperature program was officially adopted in June 2001 for the SPE-GC/MS method used on the TS-250 mass spectrometer and all subsequent work on the Saturn ion trap mass spectrometer. The updated GC temperature program, along with a lower injection temperature of 90 $^{o}$C was used for the latest set of stock solutions to get new retention times for all of the DBPs (Table 3).

In attempting to translate the retention times obtained from the older results to those found by utilizing the updated GC program, it was noted that simple linear equations can be used to approximate new retention times. During the first 23 min of the temperature programs, both results are the same because both hold the GC oven at 35 $^{o}$C for the isothermal portion of the programs. The correlation of the retention times after 23 min is not a mirror image because of the differences in ramp rates between the two temperature programs (see **Gas Chromatography** section above). Figure 4 shows the two linear approximations that can be used for estimating the new GC retention times. The equation $y = 0.9972x + 0.0699$ for the 0 to 23 minute portion of the graph is synonymous with $y = x$, with a very small offset.

**Table 3. VG TS-250 mass spectrometer quantitation ions for selected ion monitoring and elution order before and after update to GC program**

| Compound | Abbreviation | Quantitation m/z | Confirmation m/z | TS-250 Retention Time, Minutes (MtBE, 551.1 GC Program) | TS-250 Retention Time, Minutes (MtBE, Updated GC Program) |
|---|---|---|---|---|---|
| Chloroform | TCM | 83 | 49 | 6.80 | 6.92 |
| Dichloroacetaldehyde | DCA | 49 | 83 | 7.04 | 7.10 |
| Chloroacetonitrile | CAN | 75 | 77 | 8.36 | 8.47 |
| Chloropropanone | CP | 43 | 49 | 9.11 | 9.12 |
| Carbon Tetrachloride | CT | 117 | 49 | 9.38 | 9.47 |
| Trichloroacetonitrile | TCAN | 108 | 49 | 9.79 | 9.85 |
| Dichloroacetonitrile | DCAN | 74 | 49 | 11.42 | 11.38 |
| Bromodichloromethane | BDCM | 83 | 79 | 11.69 | 11.73 |
| Chloronitromethane | CNM | 49 | N/A | ----- | 12.42 |
| Bromochloroacetaldehyde | BCA | 49 | 130 | 12.57 | 12.57 |
| 1,1-Dichloropropanone | DCP | 43 | 93 | 14.06 | 14.08 |
| Dichloronitromethane | DCNM | 83 | N/A | 15.01 | 14.95 |
| Bromoacetonitrile | BAN | 119 | 79 | 16.16 | 16.10 |
| Chloropicrin | TCNM | 117 | 49 | 21.83 | 21.83 |
| Bromodichloroacetonitrile | BDCAN | 108 | 154 | 21.90 | 21.92 |
| Dibromochloromethane | DBCM | 127 | 91 | 22.68 | 22.73 |
| Bromonitromethane | BNM | 93 | 79 | 23.25 | 23.10 |
| Bromochloroacetonitrile | BCAN | 74 | N/A | 23.29 | 23.52 |
| Dichloroiodomethane | DCIM | 83 | 127 | 25.25 | 26.67 |
| Bromochloronitromethane | BCNM | 129 | 79 | 26.03 | 28.05 |
| 1,1,1-Trichloropropanone | 1,1,1-TCP | 43 | 83 | 27.08 | 30.00 |
| 1,3-Dichloropropanone | 1,3-DCP | 77 | 49 | 27.80 | 31.38 |
| Bromoform | TBM | 173 | 91 | 28.75 | 33.12 |
| Dibromoacetonitrile | DBAN | 118 | 79 | 29.05 | 33.88 |
| Bromodichloronitromethane | BDCNM | 163 | 49 | ----- | 33.87 |
| Dibromochloroacetonitrile | DBCAN | 154 | 74 | 29.32 | 34.28 |
| 1,1-Dibromopropanone | 1,1-DBP | 43 | 173 | 29.66 | 34.88 |
| Bromochloroiodomethane | BCIM | 127 | 175 | 29.80 | 35.18 |
| Dibromonitromethane | DBNM | 173 | 43 | 30.10 | 35.93 |
| 1-Bromo-1,1-dichloropropanone | 1,1,1-BDCP | 43 | 127 | 30.88 | 37.45 |
| 1,1,3-Trichloropropanone | 1,1,3-TCP | 77 | 83 | 31.22 | 38.25 |
| Tribromochloromethane | TBCM | 207 | 79 | ----- | 39.10 |
| Dibromochloronitromethane | DBCNM | 207 | 79 | ----- | 40.92 |
| Dibromoiodomethane | DBIM | 173 | 127 | 32.68 | 41.17 |
| Tribromoacetaldehyde | TBA | 251 | 173 | 32.75 | 41.40 |
| Tribromoacetonitrile | TBAN | 198 | 79 | 32.82 | 41.53 |
| Benzyl chloride | BC | 91 | N/A | 33.09 | 42.22 |
| Chlorodiiodomethane | CDIM | 175 | 127 | 33.36 | 42.62 |
| 1,1,3,3-Tetrachloropropanone | 1,1,3,3-TeCP | 83 | N/A | 33.46 | 43.00 |
| 1,1,1,3-Tetrachloropropanone | 1,1,1,3-TeCP | 77 | 49 | 33.70 | 43.53 |
| Bromopicrin | TBNM | 251 | 91 | 35.36 | 46.48 |
| Bromodiiodomethane | BDIM | 219 | 127 | 35.94 | 47.42 |
| 1,1,1-Tribromopropanone | 1,1,1-TBP | 43 | 251 | 36.14 | 47.90 |
| 1,1,3-Tribromopropanone | 1,1,3-TBP | 121 | 93 | 37.63 | 50.70 |
| Iodoform | TIM | 127 | 267 | 38.31 | 51.47 |
| 1,1,3,3-Tetrabromopropanone | 1,1,3,3-TeBP | 120 | 173 | 40.48 | 53.75 |

The interconversion between the two GC programs was helpful for determining where peaks would appear in a chromatogram, and it could be used to check the location of new peaks or impurities. The software method used for processing all SIM data was updated on 6/5/01 to reflect these new retention times, as well as the new correction factors for the latest set of stock solutions.

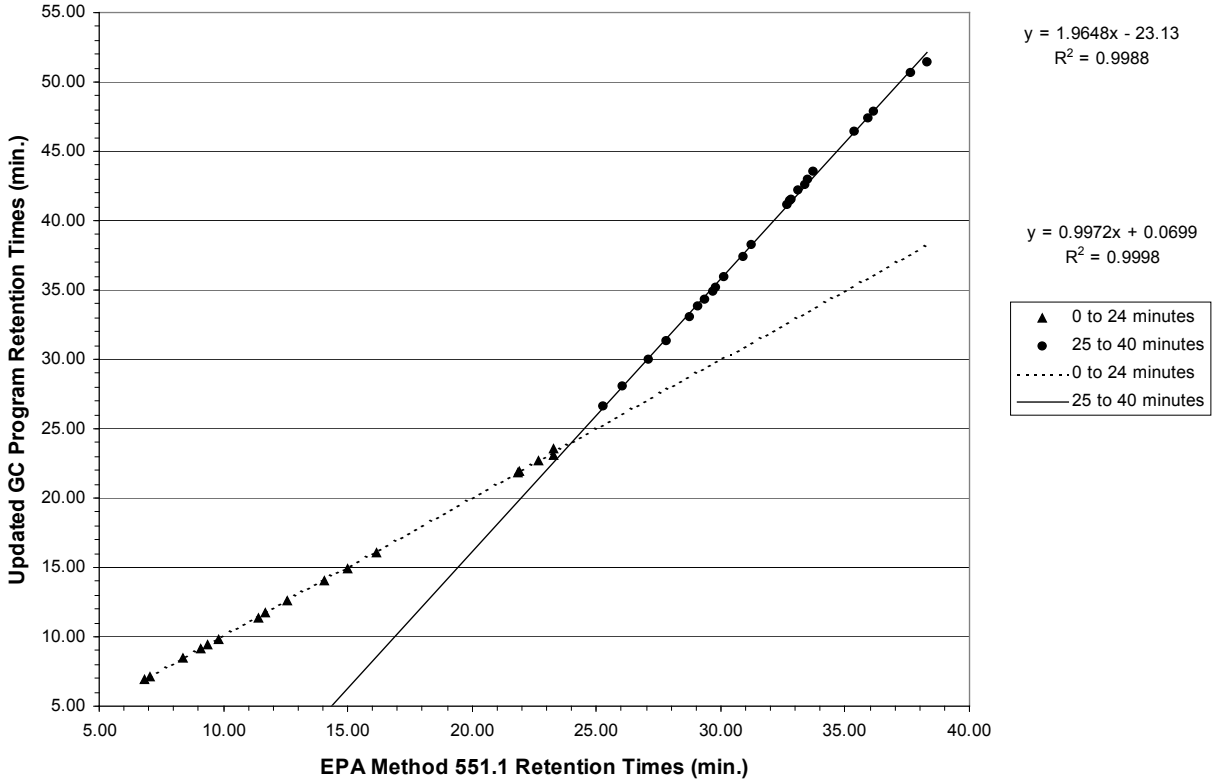


**Figure 4. Correlation of retention times before and after GC program update.**

## Problematic Compounds

All subsequent work utilized the DB-1 column for compound separation. Chloronitromethane was found to co-elute with bromochloroacetaldehyde (and trichloroacetaldehyde). There was no solution available at this time (Figure 5). It may be possible to analyze for bromochloroacetaldehyde using only m/z 130 at about 40% of the sensitivity of the m/z 49 peak. There was not, however, sufficient quantities of bromochloroacetaldehyde to warrant further methods development on the bromochloroacetaldehyde and trichloroacetaldehyde co-elution.

Chloropicrin co-eluted with bromodichloroacetonitrile. Selection of different mass channels can eliminate this conflict (Figure 6). Bromodichloroacetonitrile and trichloronitromethane can be separated on the DB-5 column. The analysis of bromodichloroacetonitrile by SPE-GC/MS was later dropped because it required ammonium chloride for a quenching agent and preservative.

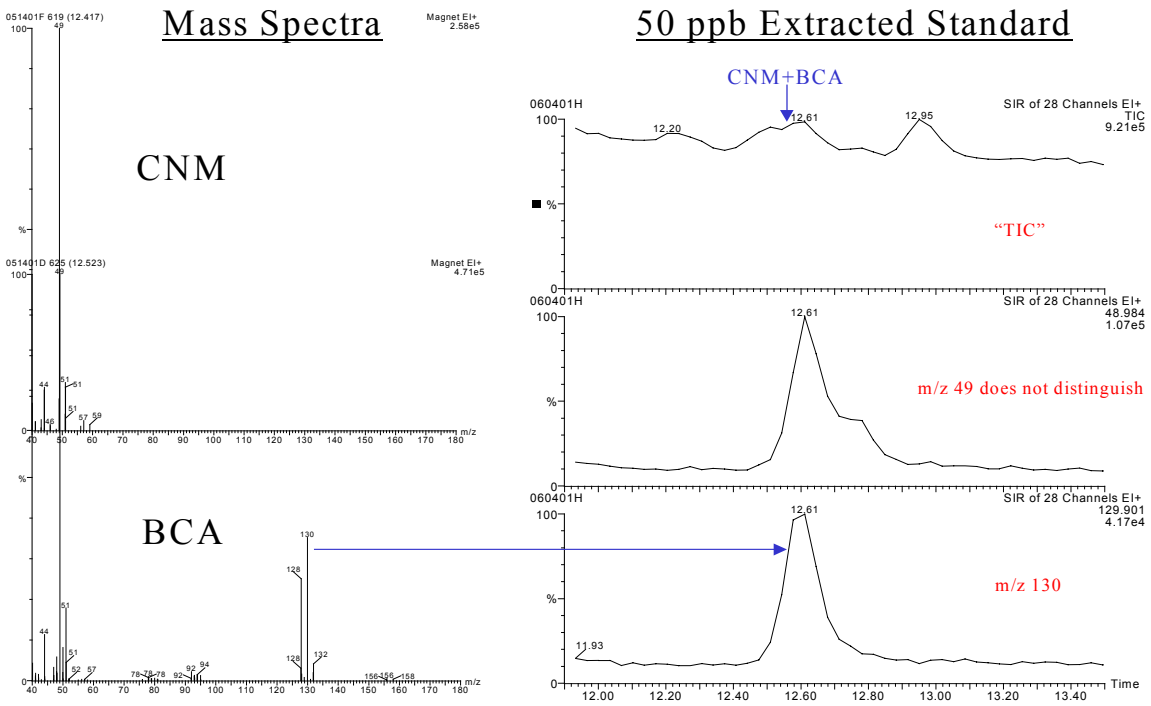


**Figure 5. Chloronitromethane (CNM) co-elutes with bromochloroacetaldehyde (BCA) (which co-elutes with trichloroacetaldehyde (TCA)). Chloronitromethane is not amenable to SPE-GC/MS analysis.**

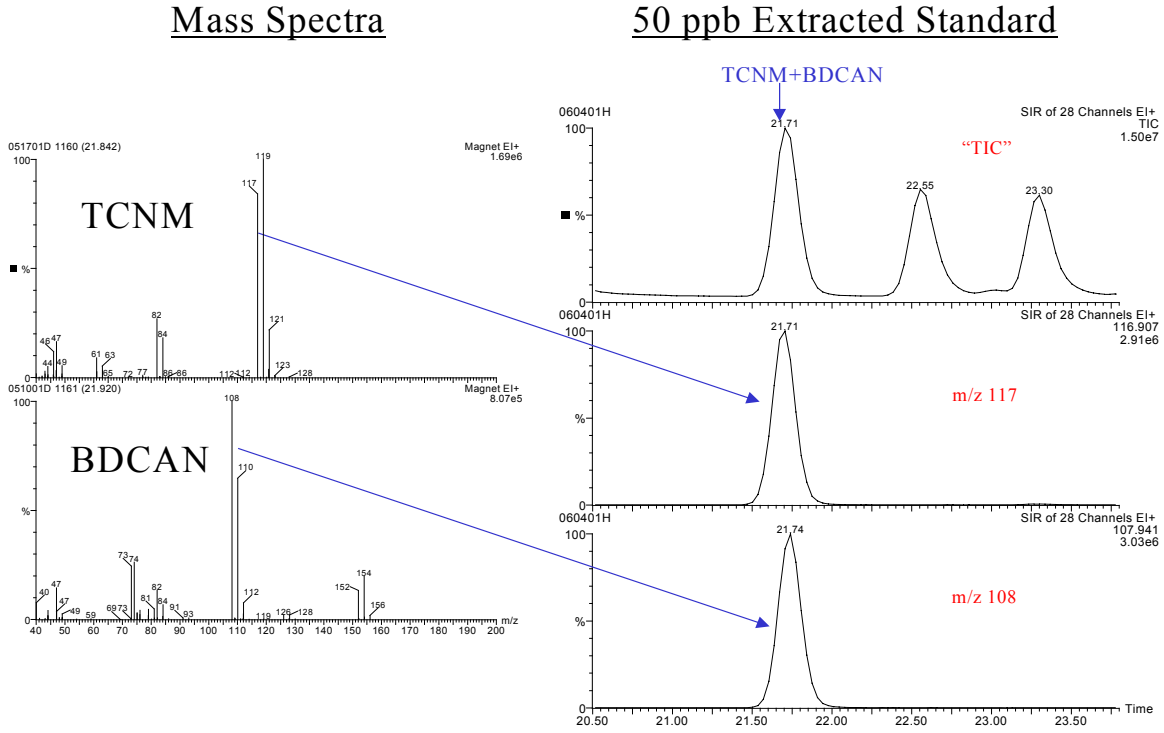


**Figure 6. Chloropicrin (TCNM) co-elutes with bromodichloroacetonitrile (BDCAN). Both are amenable to SPE-GC/MS analysis.**

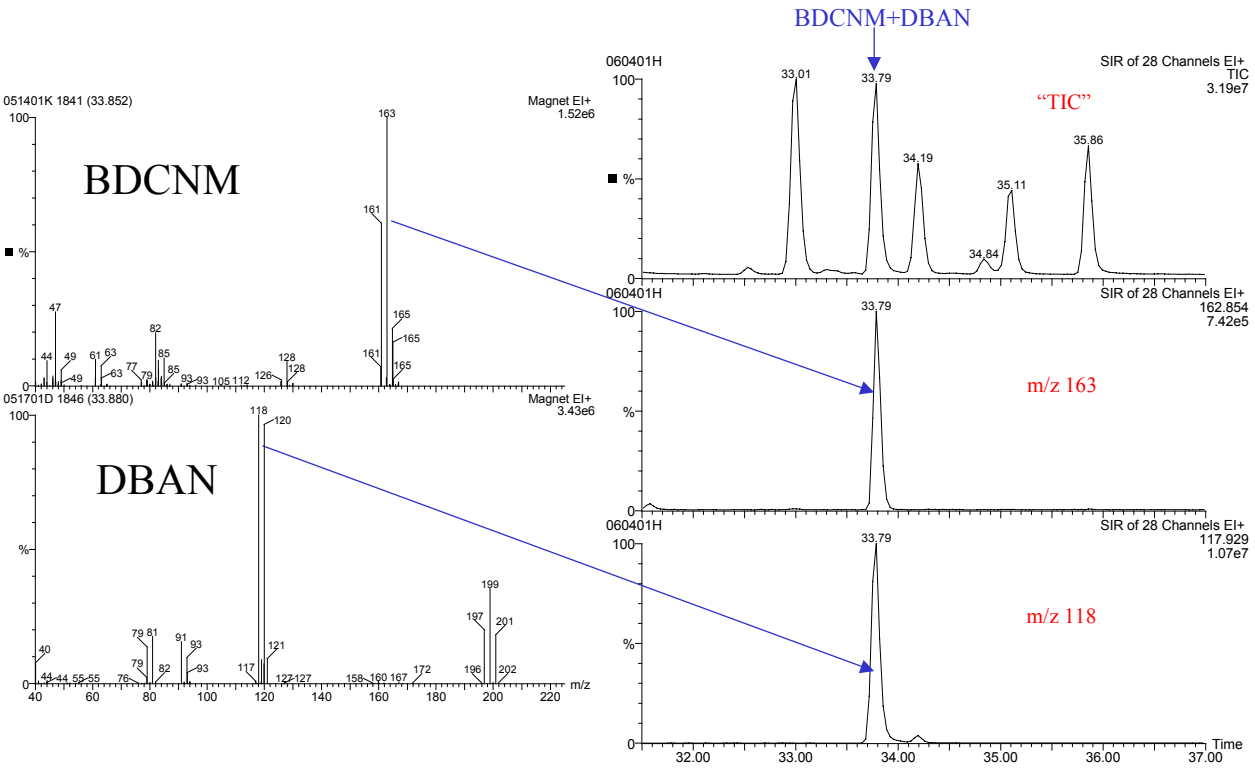


**Figure 7. Bromodichloronitromethane (BDCNM) co-elutes with dibromoacetonitrile (DBAN). Both are amenable to SPE-GC/MS analysis.**

Bromodichloronitromethane co-eluted with dibromoacetonitrile. Selection of alternate mass channels eliminates a conflict (Figure 7). However, bromodichloronitromethane was later dropped from the SPE method because it too required ammonium chloride as a quenching agent and preservative.

## Holding Study

As was stated in the **Early Observations** section of this chapter, certain heavier haloacetonitriles and halonitromethanes showed consistently poor quantitation in earlier work on this project. Before the final year of sampling was to begin, it was necessary to revisit the choice of ascorbic acid as a general quenching agent and preservative for all DBPs that were being studied by SPE, LLE, P&T, and SPME methods. Many of these compounds were not available during the initial methods development period. Thus, an experiment was carried out to evaluate the stability of DBPs stored with ascorbic acid at a pH of 3.5.

The results were surprising because it was discovered that six compounds were not amenable to this ascorbic acid/pH 3.5 combination. To summarize the results by DBP class:

| | |
|---|---|
| THMs - | No problems through Day 21. |
| Iodo-THMs - | No problems through Day 21. |
| Haloacetonitriles - | No problems through Day 21, except bromodichloro-, dibromochloro-, and tribromoacetonitrile showed no recovery between Day 0 and Day 3 (Figure 8). |
| Chloropropanones - | No problems through Day 21. 1,1-Dichloropropanone was difficult to quantitate. |
| Bromopropanones - | No problems through Day 21. 1,1,3-Tribromopropanone had a slow decay. |
| Halonitromethanes - | No problems through Day 21, except Bromodichloronitromethane, dibromochloronitromethane, and tribromonitromethane showed no recovery. |
| Haloacetaldehydes - | Difficult to quantitate. Tribromoacetaldehyde had fast decay. |
| Miscellaneous - | Both carbon tetrachloride and benzyl chloride had slow decays. |

According to the plots of concentration vs. time (Figure 8), it appeared as if the following DBPs were highly unstable in the presence of ascorbic acid at pH 3.5: bromodichloro-, dibromochloro-, and tribromoacetonitrile, and bromodichloro-, dibromochloro-, and tribromonitromethane. Previous research has shown that trichloroacetonitrile can undergo base-catalyzed hydrolysis, but it is stable at acidic pH. The brominated versions of some of these DBPs (i.e., tribromoacetonitrile, bromodichloroacetonitrile, and dibromochloroacetonitrile) may be even more unstable and may break down in the presence of ascorbic acid. However, tribromonitromethane was stable at pH 4 in the presence of ammonium chloride, so it was possible that heavy, brominated DBPs may be stable in the presence of ammonium chloride at pH 3.5.

A new holding study was carried out to evaluate ammonium chloride as a quenching agent/preservative at pH 3.5. Ascorbic acid at pH 3.5 was tested in parallel on DBPs of interest (e.g., bromodichloro-, dibromochloro-, and tribromoacetonitrile, and bromodichloro-, dibromochloro-, and tribromonitromethane). The hypothesis was confirmed, and additional sample bottles containing ammonium chloride quenching agent/preservative were added for the LLE-GC-ECD method. These six compounds were dropped from the SPE method because of the additional work load that would have been involved in sampling and extraction.

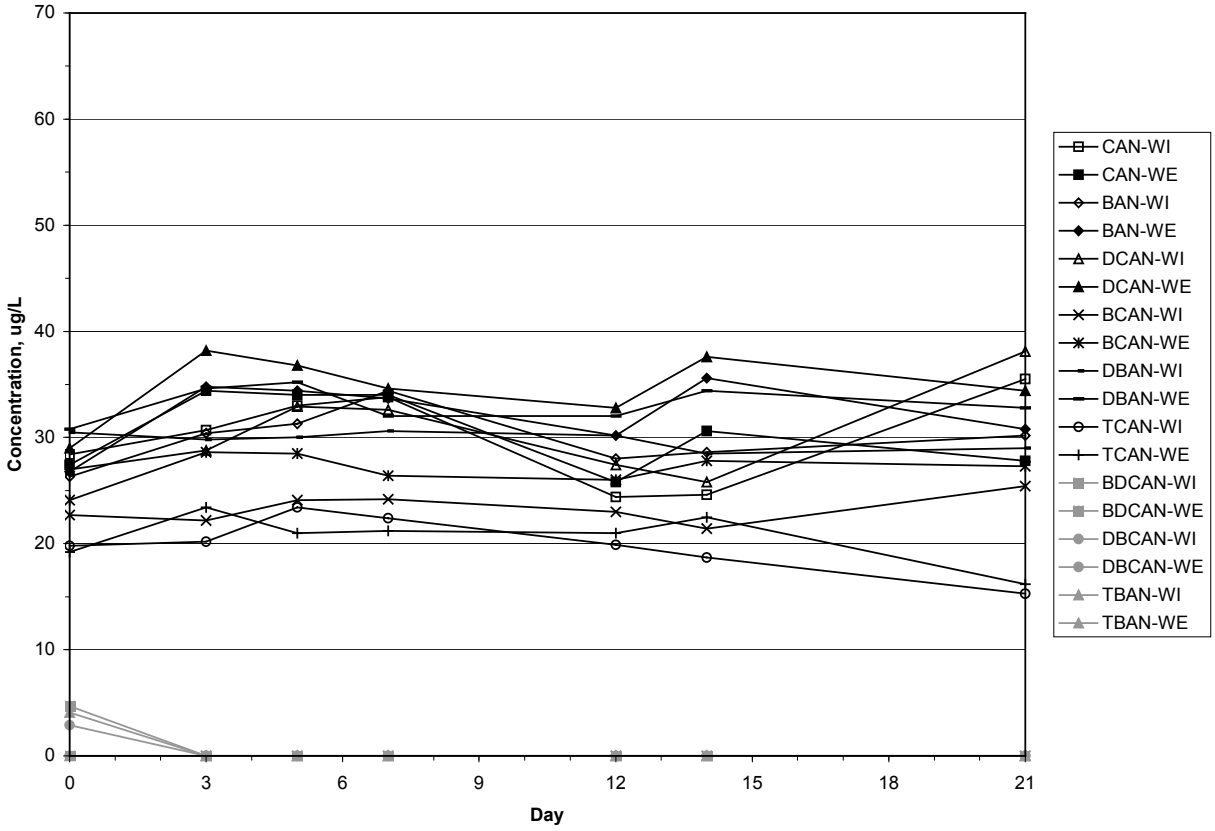


**Figure 8. Ascorbic acid/pH 3.5 holding study results for haloacetonitriles (Weymouth filtration plant influent and effluent).**

## Migration to Saturn Ion Trap Mass Spectrometer

The SPE method was implemented on the ion trap mass spectrometer as a backup system in the event that the TS-250 mass spectrometer would become unusable for the project. If, at the end of this additional methods development period, the ion trap results were much better, then the SPE method would be permanently migrated to the Saturn 2000 ion trap mass spectrometer for all subsequent work. Restrictions to this work included: a) not using MtBE as the extraction solvent, and b) keeping the instrument as "stock" as possible for easy switch-over to purge-and-trap operation. Most of the initial testing occurred during late June 2001, when the performance of the existing DB-624 GC column and alternative solvents were tested. It was found that unless the original procedure was kept intact, from development with the TS-250 mass spectrometer, it would be difficult to achieve similar results. From previous work comparing different GC columns, a switch to the preferred DB-1 column was necessary. Because of the extra efforts involved in switching columns frequently, it was hoped that the DB-1 column could be used for both SPE and P&T analysis on the same instrument. Initial work would include optimizing some instrumental parameters, automating the system, running full calibration curves (0.5 - 30 µg/L), and injecting a suite of samples to establish a preliminary MDL. The results of this SPE work on the ion trap mass spectrometer showed that low-level detection was possible for almost all of the compounds that were part of the original SPE technique performed on the TS-250 instrument.

Results for chloroform, dichloroacetaldehyde, chloroacetonitrile, and chloropropanone could not be obtained because they co-eluted with the hexane solvent that was now part of the solvent extraction system. Of the solvents listed below, *n*-hexane was a logical choice based on the boiling point of the solvents. If the solvent is too volatile, the extraction process would become more difficult because SPE extractions occur under vacuum. Unfortunately, hexane is very non-polar and does not remove as many DBPs from the Bond Elut sorbent material. A mixed solvent system of 50:50 hexane/methylene chloride allowed full extraction of the DBPs, and, at the same time, avoided bringing MtBE and larger amounts of $MeCl_2$ into the VOC room, where they are routinely determined as part of the VOC method (Table 4).

| Solvents* | Boiling Point ($^oC$) | Comments |
|---|---|---|
| Ethyl ether | 34.6 | |
| Pentane | 36.1 | |
| Methylene chloride | 39.8 | VOC compound |
| Carbon disulfide | 46.5 | |
| Methyl *tert*-butyl ether | 55.2 | VOC compound |
| Chloroform | 61.2 | VOC compound |
| *n*-Hexane | 69.0 | |
| Benzene | 80.1 | VOC compound |
| Cyclohexane | 80.7 | |
| Iso-octane | 99.3 | |
| Toluene | 110 | VOC compound |

*Recommended for non-polar columns (100% methyl or 5% phenyl, 95% methyl)

**Compound Notes**

Dichloroacetonitrile had a co-elution problem with an unknown impurity that seemed to be present in the standards. The co-elution also occurred when MtBE was used as the extraction solvent on the TS-250 instrument, but there was not sufficient resolution to resolve the co-eluting peak from dichloroacetonitrile, and the two peaks were integrated together to produce a systematic error.

Bromonitromethane was a minor problem for quantitation because it eluted between dibromochloromethane and bromochloroacetonitrile, both of which have small m/z 93 contributions to bromonitromethane's main quantitation mass channel. On the TS-250 instrument, this problem could be solved by manually re-integrating the peaks.

Chloronitromethane and bromochloracetaldehyde were eliminated from the SPE method because of their co-elution on the DB-1 column with chloral hydrate (TCA) and each other.

**Table 4. Varian Saturn 2000 performance with 1:1 Hexane/$MeCl_2$ solvent system and updated GC program. Shaded compounds were later removed from the SPE method.**

| Compound | Saturn 2000 Retention Time Using Updated GC Program | Quantitation m/z | Confirmation m/z | Lowest Standard Estimate (Ion Trap, DB-1, Splitless) |
|---|---|---|---|---|
| Chloroform | *Blocked by solvent* | 83 | 49 | *Blocked by solvent* |
| Dichloroacetaldehyde | *Blocked by solvent* | 49 | 83 | *Blocked by solvent* |
| Chloroacetonitrile | *Blocked by solvent* | 75 | 77 | *Blocked by solvent* |
| Chloropropanone | *Blocked by solvent* | 43 | 49 | *Blocked by solvent* |
| Carbon Tetrachloride | 9.40 min. | 117 | 49 | 0.50 ppb |
| Trichloroacetonitrile | 9.69 min. | 108 | 49 | 0.50 ppb |
| Dichloroacetonitrile | 10.78 min. | 74 | 49 | 0.75 ppb |
| Bromodichloromethane | 11.15 min. | 83 | 79 | 0.75 ppb |
| Chloronitromethane | *Co-elution Problem* | 49 | N/A | *Co-elution Problem* |
| Bromochloroacetaldehyde | *Co-elution Problem* | 130 | N/A | *Co-elution Problem* |
| 1,1-Dichloropropanone | 13.19 min. | 43 | 93 | 1.0 ppb |
| Dichloronitromethane | 13.95 min. | 83 | 48 | 2.5 ppb |
| Bromoacetonitrile | 14.91 min. | 119 | 79 | ? |
| Chloropicrin | 20.14 min. | 117 | 49 | 1.0 ppb |
| Bromodichloroacetonitrile | 20.18 min. | 108 | 154 | 1.0 ppb |
| Dibromochloromethane | 20.94 min. | 127 | 208 | 0.50 ppb |
| Bromonitromethane | 21.29 min. | 93 | 79 | ? |
| Bromochloroacetonitrile | 21.64 min. | 74 | 155 | 0.50 ppb |
| Dichloroiodomethane | 25.08 min. | 83 | 127 | ? |
| Bromochloronitromethane | 26.62 min. | 129 | 79 | 0.75 ppb |
| 1,1,1-Trichloropropanone | 28.66 min. | 43 | 83 | 1.0 ppb |
| 1,3-Dichloropropanone | 30.08 min. | 77 | 49 | 1.0 ppb |
| Bromoform | 31.80 min. | 173 | 254 | 0.50 ppb |
| Dibromoacetonitrile | 32.58 min. | 118 | 79 | 0.50 ppb |
| Bromodichloronitromethane | 32.61 min. | 163 | 49 | 0.50 ppb |
| Dibromochloroacetonitrile | 33.05 min. | 154 | 74 | 0.50 ppb |
| 1,1-Dibromopropanone | 33.66 min. | 43 | 173 | 1.0 ppb |
| Bromochloroiodomethane | 33.90 min. | 127 | 175 | 0.50 ppb |
| Dibromonitromethane | 34.68 min. | 173 | 43 | 0.75 ppb |
| 1-Bromo-1,1-dichloropropanone | 36.28 min. | 43 | 127 | 2.5 ppb |
| 1,1,3-Trichloropropanone | 37.07 min. | 77 | 83 | 0.75 ppb |
| Tribromochloromethane | 37.89 min. | 207 | 79 | 0.75 ppb |
| Dibromochloronitromethane | 39.76 min. | 207 | 79 | ? |
| Dibromoiodomethane | 39.99 min. | 127 | 173 | 0.75 ppb |
| Tribromoacetaldehyde | 40.24 min. | 251 | N/A | ? |
| Tribromoacetonitrile | 40.39 min. | 198 | 79 | 0.75 ppb |
| Benzyl chloride | 41.09 min. | 91 | 126 | 0.50 ppb |
| Chlorodiiodomethane | 41.44 min. | 175 | 127 | 0.50 ppb |
| 1,1,3,3-Tetrachloropropanone | 41.88 min. | 83 | 111 | 2.5 ppb |
| 1,1,1,3-Tetrachloropropanone | 42.10 min. | 77 | 49 | 0.50 ppb |
| Bromopicrin | 43.64 min. | 251 | 172 | 2.5 ppb |
| C8-Cl Internal Standard | 44.40 min. | 91 | N/A | N/A |
| Bromodiiodomethane | 46.23 min. | 219 | 127 | 0.50 ppb |
| 1,1,1-Tribromopropanone | 46.77 min. | 43 | 251 | ? |
| 1,1,3-Tribromopropanone | 49.89 min. | 121 | 93 | 1.0 ppb |
| Iodoform | 50.69 min. | 127 | 267 | 0.50 ppb |
| 1,1,3,3-Tetrabromopropanone | 53.06 min. | 120 | 173 | ? |

1,1,1,3-Tetrachloropropanone showed an unrecoverable co-elution with an impurity late in the chromatographic run (retention time of 42.1 min.). There was no solution to this problem, so poor quality assurance (QA) data was obtained for this compound, following migration to this method.

1,1,3,3-Tetrabromopropanone (retention time of 53.1 min.) exhibited poor quantitation for standards and was the latest eluting compound of all the DBPs studied. Either 1,1,3,3-tetrabrompropanone was slowly degrading or quantitation of this compound was made difficult because of poor signal-to-noise in this section of the chromatographic run, when the GC oven was doing its final ramp to 301 $^{o}$C. The baseline rises significantly about 52 min into the run.

## Multiple Quantitation Ions

The main obstacle for quantitation of SPE results was low signal-to-noise of the chromatographic peaks. The electron capture detector is inherently more sensitive for detection for halogenated compounds (as low as 0.10 ppb). SPE and P&T are comparable for minimum reporting levels, generally 0.20 to 0.25 ppb. The peaks are often much sharper and more distinct using P&T because of a lack of solvent and full injection of the sample aliquot.

A new strategy of using multiple quantitation ions for improving SPE sensitivity was tested. In the past, the SPE method used the most optimum ion channel for high abundance and

minimal interference problems from other peaks. In this new strategy, the original quantitation ion was added to the next-largest ion that was a significant contribution to the EI mass spectrum. This provided up to a two-fold improvement for some compounds. About one-third of the compounds showed improvement, with a previous reporting level of 1.0 µg/L now becoming 0.50 µg/L.

**MDL and Sample Reporting**

All of the remaining 35 compounds gave results comparable to or better than those obtained in the past using the TS-250 instrument. In several cases, the lowest calibration standards could be dropped to 0.25 µg/L. (In previous work, the lowest calibration point was 1 µg/L, and a reasonable MDL was established at 3 µg/L).

The ten calibration standards for the Varian ion trap were at concentrations of 0.25, 0.50, 1.0, 2.5, 5.0, 7.5, 10, 15, 20, and 30 µg/L. After calibration curves had been established, the data files for 0.25 µg/L - 5.0 µg/L standards were duplicated and processed as if they were actual samples to check the accuracy and integrity of the calibration curves. Table 5 shows these results. If the reported values were within 30% of the theoretical values, then the results were designated in bold type, and the lowest, reliable values to report are shown in a shaded highlight. As an example, the results for a recent Alameda County Water District sampling on 3/19/02 showed that the values used for SPE results reporting could be set much lower than those produced from a simple MDL comparison (Table 5). Because this was such an important survey study, and real world results are often below 5 µg/L for any given DBP, it was necessary to extract all available information that we could from this SPE method.

**Success with Migration of SPE Technique to Ion Trap**

The SPE technique was successfully implemented on the Saturn 2000 ion trap mass spectrometer. Full-scan mode on the Saturn ion trap provided more mass spectral information and improved the sensitivity over the TS-250 instrument. The ion trap mass spectrometer provided full automation and overnight runs, along with more reliable operation. Because both the SPE and P&T methods used the same instrument for analysis, comparison of results was much better. Because of these advantages, the Saturn 2000 ion trap mass spectrometer was used for all subsequent samplings.

**Comparison of SPE to P&T and LLE**

The pursuit of multiple analytical techniques for the Nationwide DBP Occurrence Study led to a complementary scheme for data analysis and interpretation -- the liquid-liquid extraction technique would be the primary method used for quantitation, and other techniques such as P&T, SPE, or SPME could provide true confirmation of a compound's presence. Not all the techniques could analyze for each compound. Table 6 shows the comparison of results using SPE, P&T, and LLE techniques. The results were very consistent. Because this is only a comparison of

how SPE results compare to the other techniques, many of the compounds that were part of this study, but were not amenable to SPE, were intentionally left off the table.

**Table 5. Minimum reporting levels (MRLs) for Alameda County Water District sampled on 3/19/02. A concentration in bold represents values that lie within the ± 30% range. Shading represents the lowest reportable level for this study set.**

| Compound | Quantitation Ions | 0.25 ug/L (0.175 - 0.325) Range | 0.50 ug/L (0.350 - 0.650) Range | 1.0 ug/L (0.700 - 1.300) Range | 2.5 ug/L (1.750 - 3.250) Range | 5.0 ug/L (3.500 - 6.500) Range | Minimum Reporting Level | MDL Comparison |
|---|---|---|---|---|---|---|---|---|
| **Halomethanes** | | | | | | | | |
| BDCM | 83+85 | | 0.701 | **0.835** | **2.355** | **4.034** | 1.0 ppb | 4 ppb |
| DBCM | 127+129 | **0.229** | **0.643** | **0.860** | **2.488** | **3.910** | 0.25 ppb | 6 ppb |
| TBM | 171+173 | | 0.665 | **0.953** | **2.659** | **4.221** | 1.0 ppb | 5 ppb |
| TBCM | 207+209 | **0.219** | **0.476** | **0.818** | **2.119** | 7.445 | 0.25 ppb | 5 ppb |
| DCIM | 83+85 | **0.250** | **0.534** | **0.845** | **2.417** | **4.406** | 0.25 ppb | 4 ppb |
| BCIM | 127+129 | **0.253** | 0.665 | **0.842** | **2.316** | **4.068** | 0.25 ppb | 4 ppb |
| DBIM | 127+173 | | | **0.774** | **2.244** | **4.424** | 1.0 ppb | 3 ppb |
| CDIM | 127+175 | | **0.481** | **0.701** | **2.381** | **4.516** | 0.50 ppb | 4 ppb |
| BDIM | 219+221 | | | | **1.990** | **5.899** | 2.5 ppb | 4 ppb |
| TIM | 127+267 | | | | **1.968** | **4.014** | 2.5 ppb | 4 ppb |
| **Haloacetonitriles** | | | | | | | | |
| BAN | 119+121 | | | **1.027** | **2.450** | 8.820 | 1.0 ppb | 12 ppb |
| DCAN | 74 | | 1.095 | 0.539 | **2.876** | 3.317 | 2.5 ppb | 6 ppb |
| BCAN | 74+76 | | **0.592** | **0.842** | **2.461** | **3.963** | 0.50 ppb | 5 ppb |
| DBAN | 118+120 | | **0.544** | 0.697 | **2.370** | **3.798** | 0.50 ppb | 4 ppb |
| TCAN | 108+110 | | **0.537** | **0.793** | **2.341** | **3.708** | 0.50 ppb | 3 ppb |
| **Haloketones** | | | | | | | | |
| 1,1-DCP | 43+63+83 | | | | **2.935** | 3.351 | 2.5 ppb | 5 ppb |
| 1,3-DCP | 77+79 | | | | **2.014** | **4.154** | 2.5 ppb | 5 ppb |
| 1,1-DBP | 43+79+173 | | 0.888 | **1.012** | **2.334** | **4.229** | 1.0 ppb | 5 ppb |
| 1,1,1-TCP | 43+97+125 | | **0.595** | **1.031** | **2.961** | **4.024** | 0.50 ppb | 4 ppb |
| 1,1,3-TCP | 77+83 | | | | **2.441** | **3.504** | 2.5 ppb | 7 ppb |
| 1,1,1-BDCP | 43+97+125 | | | **1.119** | **2.949** | **3.953** | 1.0 ppb | 4 ppb |
| 1,1,1-TBP | 43+79+251 | | | | **1.989** | **4.235** | 2.5 ppb | 9 ppb |
| 1,1,3-TBP | 121+123 | | | | | **3.848** | 5.0 ppb | 11 ppb |
| 1,1,3,3-TeCP | 83+85 | | | | **1.830** | **3.505** | 2.5 ppb | 8 ppb |
| 1,1,1,3-TeCP | 77+79 | | | | | | >> 5 ppb | 12 ppb |
| 1,1,3,3-TeBP | 120+122 | | | | | | >> 5 ppb | 8 ppb |
| **Haloacetaldehyde** | | | | | | | | |
| TBA | 172+173 | | | | **2.543** | **6.380** | 2.5 ppb | 8 ppb |
| **Halonitromethanes** | | | | | | | | |
| BNM | 95 | | | | | **5.092** | 5.0 ppb | 10 ppb |
| DCNM | 83+85 | 0.401 | 0.678 | **1.083** | **2.111** | **3.778** | 1.0 ppb | 10 ppb |
| BCNM | 127+129 | | | | | **4.220** | 5.0 ppb | 8 ppb |
| DBNM | 171+173 | | **0.640** | **1.039** | **2.250** | **3.999** | 0.50 ppb | 7 ppb |
| TCNM | 117+119 | | **0.509** | **0.923** | **2.473** | **4.095** | 0.50 ppb | 4 ppb |
| **Misc. Compounds** | | | | | | | | |
| CT | 117+119 | | | **1.035** | **1.978** | **6.515** | 1.0 ppb | 4 ppb |
| BC | 91+126 | **0.192** | **0.552** | **0.841** | **2.138** | 7.811 | 0.25 ppb | 4 ppb |
| 1,1,2,2-TeBCE | 141+299 | | | | 1.463 | **5.821** | 5.0 ppb | Not Available |

**Table 6. Comparison of results for SPE, P&T, and LLE analysis for Alameda County Water District. Patterned boxes denote that the compound was not reported for that method.**

| Alameda County Water District 3/19/02 | MRL | Treated Tank Effluent (MSJWTP) | | | Finished Water (MSJWTP) | | | Dist. System/Average (MSJWTP) | | | SDS Average (MSJWTP) | | | Clearwell Effluent (TP2) | | | Finished Water (TP2) | | | Dist. System/Average (TP2) | | | SDS Average (TP2) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | ug/L | SPE ug/L | P&T ug/L | LLE ug/L | SPE ug/L | P&T ug/L | LLE ug/L | SPE ug/L | P&T ug/L | LLE ug/L | SPE ug/L | P&T ug/L | LLE ug/L | SPE ug/L | P&T ug/L | LLE ug/L | SPE ug/L | P&T ug/L | LLE ug/L | SPE ug/L | P&T ug/L | LLE ug/L | SPE ug/L | P&T ug/L | LLE ug/L |
| **Halomethanes** | | | | | | | | | | | | | | | | | | | | | | | | | |
| Bromodichloromethane | 1.0 | 17.32 | 17.12 | N/A* | 22.91 | 19.27 | N/A* | 19.77 | 21.91 | N/A* | 26.84 | 23.52 | N/A* | 2.10 | 2.02 | N/A* | 2.40 | 2.84 | N/A* | 3.74 | 4.93 | N/A* | 4.18 | 4.54 | N/A* |
| Dibromochloromethane | 0.25 | 7.85 | 4.8 | N/A* | 9.62 | 5.34 | N/A* | 8.99 | 5.65 | N/A* | 9.99 | 5.78 | N/A* | 2.38 | 0.97 | N/A* | 2.87 | 1.78 | N/A* | 5.25 | 3.51 | N/A* | 5.46 | 3.38 | N/A* |
| Bromoform | 1.0 | (0.78) | 0.67 | N/A* | (0.91) | 0.69 | N/A* | (0.90) | 0.82 | N/A* | (0.92) | 0.84 | N/A* | (0.65) | [0.49] | N/A* | (0.79) | 0.76 | N/A* | 2.21 | 2.3 | N/A* | 2.43 | 2.37 | N/A* |
| Tribromochloromethane | 0.25 | | | | | | | | | | | | | | | | | | | | | | | | |
| Dichloroiodomethane | 0.25 | 1.35 | 1.61 | 3.7 | 1.75 | 2.04 | 2.6 | 2.02 | 3.07 | 1.8 | 2.41 | 3.26 | 2.3 | | | 2.0 | | | 2.5 | | | 1.4 | | | |
| Bromochloroiodomethane | 0.25 | 0.88 | 1.3 | 1.6 | 1.00 | 1.5 | 1.1 | 0.87 | 1.2 | 1.3 | 1.08 | 1.66 | 1.5 | | | | | | | + | | | + | | |
| Dibromoiodomethane | 1.0 | + | 0.51 | | + | 0.6 | | + | [0.44] | | (0.34) | 0.54 | | | | | | | | | | | | | |
| Chlorodiiodomethane | 0.50 | + | | 0.9 | + | | 0.7 | + | | 1.1 | + | | 1.2 | | | | | | | | | | | | |
| Bromodiiodomethane | 2.5 | | | | | | | | | | | | | | | | | | | | | | | | |
| Iodoform | 2.5 | | | | | | | | | | | | | | | | | | | | | | | | |
| **Haloacetonitriles** | | | | | | | | | | | | | | | | | | | | | | | | | |
| Bromoacetonitrile | 1.0 | | | | | | | | | | | | | | | | | | | | | | | | |
| Dichloroacetonitrile | 2.5 | (0.96) | 1.35 | 7.5 | (0.97) | 1.41 | 7.2 | (1.20) | 1.43 | 6.6 | (1.49) | 1.58 | 7.7 | | | 0.7 | | | 0.7 | | | 1.3 | | | 1.2 |
| Bromochloroacetonitrile | 0.50 | 0.95 | | 1.1 | 0.95 | | 1.8 | 1.10 | | 1.0 | 1.17 | | 1.2 | + | | | + | | 0.8 | (0.41) | | 2.2 | (0.34) | | 1.6 |
| Dibromoacetonitrile | 0.50 | (0.28) | | 0.7 | 0.70 | | 1.1 | (0.36) | | 0.7 | (0.33) | | 0.8 | + | | 0.5 | + | | 0.6 | (0.36) | | 1.1 | (0.28) | | 0.4 |
| Trichloroacetonitrile | 0.50 | | | | | | | | | | | | | | | | | | | | | | | | |
| **Haloketones** | | | | | | | | | | | | | | | | | | | | | | | | | |
| 1,1-Dichloropropanone | 2.5 | | 1.06 | 3.3 | (0.72) | 0.92 | 2.1 | | 0.52 | 1.9 | | [0.49] | 2.0 | | | 1.2 | | | 1.1 | | | 1.5 | | 0.56 | 2.4 |
| 1,3-Dichloropropanone | 2.5 | | | | | | | | | | | | | | | 0.2 | | | | | | | | | |
| 1,1-Dibromopropanone | 1.0 | | | | | | | | | | | | | | | | | | | | | | | | |
| 1,1,1-Trichloropropanone | 0.50 | 1.46 | 3.68 | 5.6 | 2.01 | 3.71 | 6.0 | 1.40 | 2.32 | 4.2 | 1.66 | 2.42 | 4.3 | + | | 0.9 | (0.28) | | 0.8 | | | 0.6 | | | 0.3 |
| 1,1,3-Trichloropropanone | 2.5 | | | | | | | | | | | | | | | | | | | | | | | | |
| 1,1,1-Bromodichloropropanone | 1.0 | + | | | + | | 0.9 | | | | | | | | | 0.1 | | | 0.2 | | | | | | |
| 1,1,1-Tribromopropanone | 2.5 | | | | | | | | | | | | | | | | | | | | | | | | |
| 1,1,3-Tribromopropanone | 5.0 | | | | | | 0.1 | | | | | | | | | 0.5 | | | | | | | | | |
| 1,1,3,3-Tetrachloropropanone | 2.5 | | | | | | | | | | | | | | | | | | | | | | | | |
| 1,1,1,3-Tetrachloropropanone | >> 5 | | | | | | | | | | | | | | | | | | | | | | | | |
| 1,1,3,3-Tetrabromopropanone | >> 5 | | | | | | | | | | | | | | | | | | | | | | | | |
| **Haloacetaldehydes** | | | | | | | | | | | | | | | | | | | | | | | | | |
| Tribromoacetaldehyde | 2.5 | | | 0.4 | | | 0.1 | | | | | | | | | 0.8 | | | 0.5 | | | | | | |
| **Halonitromethanes** | | | | | | | | | | | | | | | | | | | | | | | | | |
| Bromonitromethane | 5.0 | | | | | | | | | | | | | | | | | | | | | | | | |
| Dichloronitromethane | 1.0 | + | | 0.3 | + | | 0.2 | + | | 0.2 | + | | 0.3 | | | | | | | + | | 0.2 | | | 0.3 |
| Bromochloronitromethane | 5.0 | | | | | | 0.3 | | | | | | | | | | | | 0.1 | | | 0.2 | | | |
| Dibromonitromethane | 0.50 | | | | | | | | | | | | | | | | | | 0.1 | | | | | | |
| Trichloronitromethane | 0.50 | (0.25) | | 0.3* | + | | 0.6* | (0.40) | | 1.2* | 0.53 | | 1.5* | | | | | | | + | | 0.8* | (0.33) | | 0.9* |
| **Misc. Compounds** | | | | | | | | | | | | | | | | | | | | | | | | | |
| Carbon tetrachloride | 1.0 | | | | | | | | | | | | | | | | | | | | | | | | |
| Benzyl Chloride | 0.25 | | | | | | | | | | | | | | | | | | | | | | | | |
| 1,1,2,2-Tetrabromochloroethan | 5.0 | | | | | | | | | | | | | | | | | | | | | | | | |

+ Compound is present but could not be quantitated.
* High spike recovery.

## CONCLUSIONS

There was no one universal method that could be used to analyze all targeted DBPs. LLE-GC-ECD is the most universal of all the techniques, but it does not provide the definitive results that a mass spectrometric technique provides. Of the two mass spectrometry techniques examined (P&T-GC/MS and SPE-GC/MS), P&T-GC/MS excelled at measuring volatiles and benefited from being a solvent-less technique. SPE, on the other hand, can make use of a variety of sorbents to target specific families of compounds or to provide general screening results, as was the case for this study.

The solid phase extraction technique was developed to incorporate as many compounds as possible. To this end, we achieved our goal. In future work, we hope to improve upon the technique by taking advantage of many new sorbents that have appeared on the market, which offer improved extraction efficiencies that should provide lower detection limits. We are also pursuing an on-line solid phase extraction apparatus that will remove the need for an operator to extract the cartridges by hand, which should improve reproducibility. A fully automated on-line SPE system would offer the flexibility to screen many compounds, ranging from volatiles to semi-volatiles, with full mass spectrometric detection and limited user intervention.